10/583182
IAP12 Rec'd PCT/PTO 16 JUN 2006

Description

ACRYLIC SHRINKABLE FIBER AND METHOD FOR PRODUCTION THEREOF

Technical Field

The present invention relates to a dyeable highly shrinkable acrylic fiber having a high shrinkage percentage even after dyeing, and to a process for producing the same.

Background Art

Conventionally, acrylic fibers have texture like animal hair, and are used in artificial fur goods such as toys and clothes due to their characteristics. In particular, artificial fur products have a down hair part composed of a shrinkable fiber and a guard hair part composed of a non-shrinkable fiber in appearance in many cases, so as to provide the artificial fur products with fur texture and natural appearance. Since pile fabrics are required to have appearance characteristics, shrinkable fibers are also required to have various hues. However, only shrinkable fibers with limited kinds of hues which are colored in the spinning process have been provided as shrinkable fibers.

The acrylic shrinkable fiber of the present invention after the dyeing process is treated with dry

heat in the tentering process in pile processing to shrink. So far, a highly shrinkable acrylonitrile synthetic fiber has been obtained from a copolymer composed of 30 to 58 wt% of acrylonitrile, 70 to 42 wt% of vinylidene chloride and vinyl chloride and 0 to 10 wt% of one or more ethylenically unsaturated monomers (Japanese Patent Laid-Open No. 60-110911). According to the knowledge of the present inventors, the above shrinkable fiber shrinks when dyed at 70°C or more, and does not considerably shrinks by heat of the tentering process in pile processing in which an adhesive is caused to adhere to the pile back surface and dried. Further, the shrinkable fiber can be prevented from shrinking when dyed at less than 70°C and shrink by heat of the tentering process, but cannot be sufficiently dyed.

In order to improve low-temperature dyeability, a dyeable shrinkable fiber is obtained by mixing 95 to 60 parts by weight of a polymer (I) comprising 40 wt% or more of acrylonitrile and 20 to 60 wt% of vinylidene chloride and a sulfonic acid-containing monomer with 5 to 40 parts by weight of a highly dyeable polymer (II) comprising 30 to 75 wt% of acrylonitrile and 25 to 70 wt% of methyl acrylate (Japanese Patent No. 2566890). The resulting shrinkable fiber has improved dyeability at a low temperature to have a suppressed dyeing shrinkage percentage, and can shrink at 20% or more after dyeing. It is assumed that the polymer (I) and the polymer (II)

are compatible with each other in the shrinkable fiber. According to the knowledge of the present inventors, when the polymer (I) and the polymer (II) are compatible with each other, the polymer (II) having properties to improve dyeability at a low temperature as well as properties to reduce heat resistance is continuously present in the fiber. For this reason, the polymer (II) highly affects the shrinkage behavior of the fiber, and it is difficult to suppress the dyeing shrinkage percentage even at a low dyeing temperature. When the fiber highly shrinks when dyed, the shrinkage percentage after dyeing is made small. When the fiber shrinks during dyeing, the fiber packing density in a dyeing machine is made small to generate a by-pass which causes dyeing nonuniformity. Further, the fiber has drawbacks in that, for example, it is difficult to stretch crimps generated during shrinkage in the polishing process in pile processing. Thus a pile fabric having desired appearance and texture cannot be provided. These problems are still to be solved, and a dyeable acrylic shrinkable fiber that only slightly shrinks when dyed and has a high shrinkage percentage even after dyeing has not been provided.

Disclosure of the Invention

Accordingly, an object of the present invention is to solve the above problems of the prior art and to provide a dyeable acrylic shrinkable fiber that only

slightly shrinks when dyed and has a high shrinking percentage even after dyeing.

As a result of extensive studies, the present inventors have found that a dyeable acrylic shrinkable fiber that only slightly shrinks when dyed and has a high shrinkage percentage after dyeing can be provided by spinning an incompatible spinning solution.

Specifically, the present invention relates to a dyeable acrylic shrinkable fiber produced from a spinning solution comprising a polymer composition in which 50 to 99 parts by weight of a polymer (A) comprising 40 to 80 wt% of acrylonitrile, 20 to 60 wt% of a halogen-containing monomer and 0 to 5 wt% of a sulfonic acid-containing monomer is mixed with 1 to 50 parts by weight of a polymer (B) comprising 5 to 70 wt% of acrylonitrile, 20 to 94 wt% of other copolymerizable monomer and 1 to 40 wt% of a sulfonic acid-containing monomer, wherein the polymer (A) and the polymer (B) are incompatible with each other.

The other copolymerizable monomer in the acrylic shrinkable fiber is preferably an acrylic acid ester.

The other copolymerizable monomer in the acrylic shrinkable fiber is preferably an acrylic acid ester.

The spinning solution in the acrylic shrinkable fiber is preferably phase separated into particles having a particle size of 0.1 to 30 μm.

The acrylic shrinkable fiber preferably has a dyeing shrinkage percentage at 80°C or less of 10% or less and a shrinkage percentage after dyeing of 20% or more.

The acrylic shrinkable fiber preferably has a relative saturation value at 60°C or more of 0.1 or more and a relative saturation value at 70°C or more of 0.8 or more.

A process for producing the acrylic shrinkable fiber preferably comprises carrying out relaxation treatment at 1 to 20%.

The polymer (A) used for producing the acrylic shrinkable fiber of the present invention is a polymer comprising 40 to 80 wt% of acrylonitrile, 20 to 60 wt% of a halogen-containing monomer and 0 to 5 wt% of a sulfonic acid-containing monomer.

In the polymer (A), acrylonitrile is preferably used in an amount of 40 to 80 wt%. If the acrylonitrile content is less than 40 wt%, the resulting fiber has too low heat resistance. If the acrylonitrile content is more than 80 wt%, the fiber has too high heat resistance, and thus cannot have sufficient dyeability and shrinkage percentage. The halogen-containing monomers in the polymer (A) of the present invention are preferably vinyl halides and vinylidene halides typified by vinyl chloride, vinylidene chloride, vinyl bromide and vinylidene bromide. These may be used singly or in a mixture of two or more. The halogen-containing monomer is preferably used in the

polymer (A) in an amount of 20 to 60 wt%. If the content of the halogen-containing monomer is more than 60 wt%, the fiber is too hydrophobic, and thus cannot have sufficient dyeability. If less than 20 wt%, the fiber of rough touch giving uncomfortable feeling is produced.

The sulfonic acid-containing monomer in the polymer (A) of the present invention is preferably allylsulfonic acid, methallylsulfonic acid, styrenesulfonic acid, isoprenesulfonic acid, 2-acrylamido-2-methylpropanesulfonic acid, or a metal salt or amine salt thereof. These may be used singly or in a mixture of two or more. In the polymer (A) of the present invention, the content of the sulfonic acid-containing monomer is preferably 0 to 5 wt%. If the content is more than 5 wt%, voids or agglutination are formed in the fiber, and the fiber has decreased strength.

The polymer (B) used for producing the acrylic shrinkable fiber of the present invention is a polymer comprising 5 to 70 wt% of acrylonitrile, 20 to 94 wt% of another copolymerizable monomer and 1 to 40 wt% of a sulfonic acid-containing monomer.

In the polymer (B), acrylonitrile is preferably used in an amount of 5 to 70 wt%. If the acrylonitrile content is more than 70 wt%, the fiber has too high heat resistance, and thus cannot have sufficient dyeability and shrinkage percentage.

Preferable examples of the other copolymerizable monomer in the polymer (B) of the present invention include acrylic acid, methacrylic acid and their lower alkyl esters, N- or N,N-alkyl substituted aminoalkyl esters or glycidyl esters; acrylamide, methacrylamide and their N- or N,N-alkyl substituted products; anionic vinyl monomers such as carboxyl group-containing vinyl monomers typified by acrylic acid, methacrylic acid and itaconic acid and their sodium, potassium or ammonium salts; cationic vinyl monomers typified by quaternary aminoalkyl esters of acrylic acid or methacrylic acid; vinyl group-containing lower alkyl ethers; vinyl group-containing lower carboxylic acid esters typified by vinyl acetate; vinyl halides and vinylidene halides typified by vinyl chloride, vinylidene chloride, vinyl bromide and vinylidene bromide; and styrene. These monomers may be used singly or in a mixture of two or more. The content of the other copolymerizable monomer is preferably 20 to 94 wt%. If the content is less than 20 wt%, the fiber has too high heat resistance, and thus cannot have sufficient dyeability. It is preferable to use an acrylic acid ester as the other copolymerizable monomer particularly in terms of dyeability. Preferable examples of the acrylic acid ester include methyl acrylate, ethyl acrylate and butyl acrylate. These monomers may be used singly or in a mixture of two or more.

The sulfonic acid-containing monomer in the polymer (B) is preferably allylsulfonic acid, methallylsulfonic acid, styrenesulfonic acid, isoprenesulfonic acid, 2-acrylamido-2-methylpropanesulfonic acid, or a metal salt or amine salt thereof. These may be used singly or in a mixture of two or more. In the polymer (B) of the present invention, the content of the sulfonic acid-containing monomer is preferably 1 to 40 wt%. If the content is more than 40 wt%, voids or agglutination are formed in the fiber, and the fiber has decreased strength.

In the acrylic shrinkable fiber of the present invention, in order to improve dyeability, the total content of the sulfonic acid group-containing monomers in the polymers (A) and (B) contained in the fiber is preferably 0.1 to 10 parts by weight, and more preferably 0.2 to 5 parts by weight based on the total monomer content in the polymers (A) and (B). If the content is less than 0.1 part by weight, the fiber cannot have sufficient dyeability. If more than 10 parts by weight, voids or agglutination are formed in the fiber, and the fiber has decreased strength, undesirably. When the polymer (B) comprises 10 wt% or more of a sulfonic acid-containing monomer, the polymer (A) and the polymer (B) tend to be incompatible with each other.

The polymers (A) and (B) of the present invention can be obtained by a conventional vinyl polymerization method such as emulsion polymerization, suspension

polymerization or solution polymerization, using a known compound as initiator, for example, peroxide compound, azo compound, or various redox compounds.

The polymers (A) and (B) of the present invention are dissolved in an organic solvent, for example, acetone, acetonitrile, dimethylformamide, dimethylacetamide or dimethyl sulfoxide, or in an inorganic solvent, for example, zinc chloride, nitric acid or rhodan salt to prepare a spinning solution. Inorganic and/or organic pigment such as titanium oxide or coloring pigment, stabilizer effective for anti-corrosion, coloring spinning or weather resistance, or the like can be used for the spinning solution, insofar as spinning can be carried out without problems.

If the polymers (A) and (B) of the present invention are mixed so that the polymer (B) is less than 1 wt%, the fiber cannot have sufficient dyeability. If the polymer (B) is more than 50 wt%, voids or agglutination are formed on the fiber, and the fiber has decreased strength and dyeability, undesirably.

The term "incompatible" in the present invention preferably refers to a state in which the spinning solution is phase separated into particles having a particle size of 0.1 to 30 μm, and more preferably refers to a state in which the spinning solution is phase separated into particles having a particle size of 6 to 12 μm. In a phase separation state of particles having a

particle size of less than 0.1 μm, the fiber has a high shrinkage percentage when dyed, due to the properties of the polymer (B). In a phase separation state of particles having a particle size of more than 30 μm, voids or agglutination are formed in the fiber, and the fiber has decreased strength and dyeability, undesirably.

The acrylic shrinkage fiber of the present invention is made of a spinning solution in which the polymers (A) and (B) are incompatible with each other. Thus, the fiber is assumed to have a sea-island structure in which the polymer (B) present in a lower proportion in the polymer (A) present in a higher proportion forms like islands in the sea. Therefore, since the polymer (B) is not continuously present in the fiber, the fiber has low heat resistance but its shrinkage behavior is not remarkably affected by the polymer (B). Accordingly, a fiber made of an incompatible spinning solution can have a low dyeing shrinkage percentage as compared with a fiber made of a compatible spinning solution. Since the shrinkage percentage of the shrinkable fiber is determined according to the resin composition and the spinning method, when the fiber considerably shrinks in the dyeing process, the shrinkage percentage in the subsequent pile processing process is small. Therefore, the shrinkage percentage after dyeing can be increased by decreasing the dyeing shrinkage percentage.

Further, in the present invention, when the polymer (A) contains vinyl chloride, compatibility between the polymer (A) and the polymer (B) can be decreased.

The dyeing shrinkage percentage in the present invention is an index showing how much the fiber shrinks by dyeing, and is determined in the following manner. A fiber with a length Lo is treated with a water bath at any temperature for 60 minutes, and then the length L of the resulting fiber is measured. The dyeing shrinkage percentage is determined by the following formula.

Dyeing shrinkage percentage (%) = $((Lo - L)/Lo) \times 100$

The shrinkage percentage after dyeing in the present invention is an index showing how much the fiber shrinks after dyeing by the tentering process, and is determined in the following manner. A fiber after dyeing with a length Ldo is treated with a holding oven at 130°C for five minutes, and then the length Ld of the resulting fiber is measured. The shrinkage percentage after dyeing is determined by the following formula.

Shrinkage percentage after dyeing (%) = $((Ldo - Ld)/Ldo) \times 100$

In the process for producing the acrylic shrinkable fiber of the present invention, the spinning solution is spun through a nozzle by a conventional wet or dry spinning method, drawn, and dried. The spinning solution may be further drawn or treated with heat as necessary.

Further, the resulting fiber can be drawn at a ratio of 1.3 to 4.0 at 70 to 140°C to obtain a shrinkable fiber.

When the acrylic shrinkable fiber of the present invention has a high dyeing shrinkage percentage, it is preferable to carry out relaxation treatment at 1% or more in the fiber production process to suppress shrinkage. The relaxation treatment is preferably carried out with wet heat or dry heat at 70°C to 140°C. The dyeing shrinkage percentage can be suppressed by increasing the treatment temperature and making the relaxation percentage higher. However, since the shrinkage percentage after dyeing is also suppressed in relaxation treatment under extreme conditions, the relaxation treatment is preferably carried out at a temperature of about 110°C at 20% or less.

The acrylic shrinkable fiber of the present invention is caused to shrink in the tentering process in pile processing. The tentering process is carried out with dry heat preferably at 110 to 150°C, and typically at about 130°C. Thus, the shrinkage percentage after dyeing is measured under conditions where the fiber shrinks with dry heat at 130°C for five minutes.

The acrylic shrinkable fiber of the present invention has a high dyeing shrinkage percentage at a high dyeing temperature. Therefore, a dyeing temperature of more than 90°C is not preferable, because the dyeing shrinkage percentage is high. Further, when the fiber

considerably shrinks by dyeing, the room for shrinkage in the fiber is made small, and thus it is difficult to make the shrinkage percentage after dyeing 20% or more. If the dyeing shrinkage percentage is more than 10%, the fiber packing density in a dyeing machine is made small to generate a by-pass which tends to cause dyeing nonuniformity. Further, the fiber has drawbacks in that, for example, it is difficult to stretch crimps generated during shrinkage in the polishing process in pile processing. Thus, a pile fabric having desired appearance and texture cannot be provided. If the acrylic shrinkable fiber of the present invention has a shrinkage percentage after dyeing of less than 20%, the fiber processed into a pile fabric has a small step from the non-shrinking raw cotton, and thus the pile step (two-tone) cannot be distinguishable. Accordingly, a pile fabric having natural or well-designed appearance characteristics cannot be obtained.

The relative saturation value in the present invention is an index of dyeability of the fiber. The fiber is dyed with a supersaturation amount of Malachite Green at any temperature for 60 minutes to determine the saturation concentration of dye. The relative saturation value was determined by the saturation concentration of dye. The saturation concentration of dye and the relative saturation value were determined by the following formulas.

Saturation concentration of dye = ((Ao - A)/Ao) × 2.5)
A: Absorbance of dye bath after dyeing (wavelength: 618 nm)
Ao: Absorbance of dye bath before dyeing (618 nm)

Relative saturation value = Saturation concentration of dye × 400/463

The acrylic shrinkable fiber of the present invention can be lightly dyed at a relative saturation value of 0.1 or more. Further, since the fiber can be dyed to light to dark colors, or even black at a relative saturation value of 0.8 or more, the relative saturation value is preferably 0.8 or more.

The performance evaluation methods of test fibers will be described below in detail prior to description of examples.

(1) Phase separation state

A base dope was mixed with a blend polymer at any ratio to prepare a spinning solution. The spinning solution was observed with a phase contrast microscope (manufactured by Ario Techno Co., Ltd., ANS30). Particle sizes of ten separated blend polymer particles randomly selected were measured to determine an average. The phase separation state was evaluated based on the average.

(2) High pile test production

A shrinkable fiber was blended with a non-shrinkable fiber, and the blend fiber was humidity conditioned. The fiber was prepared into a card sliver through an opener

and a card. Next, the carded sliver was subjected to sliver knitting in a high pile knitting machine, and the pile part was cut by shearing to make the pile part length uniform. Then, the pile back surface was back coated with an acrylic acid ester adhesive. Next, the adhesive was dried at 130°C for five minutes and, at the same time, the shrinkable fiber was caused to shrink. Thereafter, the pile part was finished into a high pile by carrying out polish finishing and shearing.

(3) High pile appearance evaluation

For the step pile fabric prepared in the manner described in (2), four-grade sensory evaluation of the degree of appearance characteristics, in which the step between the long pile part and the short pile part is emphasized, was carried out from the visual and sensory points of view in the following standards.

Very good: The step pile fabric has appearance characteristics in which the step between the long pile part and the short pile part is greatly emphasized.

Good: The step pile fabric has appearance characteristics in which the step between the long pile part and the short pile part is emphasized.

Fair: The step between the long pile part and the short pile part is not much emphasized in the step pile fabric.

Poor: The step between the long pile part and the short pile part almost cannot be observed in the step pile fabric.

Examples will be described below. "Part(s)" in the examples refers to "part(s) by weight" unless otherwise indicated.

Examples

(Production Example 1)

A pressure polymerization reactor having an internal volume of 20 L was charged with 200 parts of ion exchange water, 0.9 part of sodium lauryl sulfate, 0.43 part of sulfurous acid, 0.22 part of sodium hydrogensulfite, 0.001 part of iron sulfate, 4.9 parts of acrylonitrile (hereinafter referred to as AN) and 52.5 parts of vinyl chloride (hereinafter referred to as VC), and the internal atmosphere was replaced with nitrogen. The polymerization reactor was adjusted to an internal temperature of 50°C, and charged with 0.035 part of ammonium persulfate as an initiator to initiate polymerization. Polymerization was carried out for a polymerization time of 5 hours and 10 minutes while adding 42.1 parts of AN, 0.5 part of sodium styrenesulfonate (hereinafter referred to as 3S) and 0.23 part of ammonium persulfate.

Then, the unreacted VC was recovered, and the latex was removed from the polymerization reactor, salted out, treated with heat, filtered, washed with water, dehydrated, and dried to obtain a polymer 1.

Next, a pressure polymerization reactor having an internal volume of 5 L was charged with 187 parts of acetone, 47 parts of water, 40 parts of AN, 45 parts of methyl acrylate (hereinafter referred to as MA), and 15 parts of sodium 2-acrylamido-2-methylpropanesulfonate (hereinafter referred to as SAM), and the internal atmosphere was replaced with nitrogen. The polymerization reactor was adjusted to an internal temperature of 65°C, and charged with 0.5 part of 2,2'-azobis(2,4-dimethylvaleronitrile) as an initiator to initiate polymerization. The components were polymerized for two hours while adding 1.0 part of azobis in the middle of the polymerization. Then, the components were heated to 70°C and polymerized for two hours to obtain a solution of a polymer 2 having a polymer concentration of 30 wt%. The polymer 1 was dissolved in acetone to prepare a polymer 1 solution having a polymer 1 concentration of 30 wt%. The polymer 1 solution was mixed with the polymer 2 solution at a ratio of the polymer 1 to the polymer 2 of 9:1 to prepare a spinning solution. The resulting spinning solution was discharged through a spinneret with 8,500 holes having a diameter of 0.08 mm into a 30 wt% aqueous acetone solution at 25°C, then drawn at a ratio of 2.0 in a 20 wt% aqueous acetone solution at 25°C, and thereafter washed with water at 60°C. Then, the spinning solution was dried at 130°C and

further drawn at a ratio of 1.8 at 105°C to obtain a 4.4 dtex drawn yarn.

Subsequently, the resulting shrinkable fiber was crimped, cut into a 32 mm fiber, and then dyed with 0.2% omf of Maxilon Red GRL (manufactured by Ciba Specialty Chemicals, Inc.) as a dye and 0.5 g/L of UltraMT #100 (manufactured by Mitejima Chemical Co., Ltd.) as a dyeing aid at 60°C, 70°C and 80°C for 60 minutes. 70 wt% of the dyed fiber was blended with 30 wt% of a non-shrinkable raw fiber "Kanecaron (R)" RCL 12.2 dtex, 44 mm (manufactured by Kaneka Corporation) to prepare a high pile. At that time, the pile part was cut into a pile length of 15 mm by shearing after sliver knitting, and cut into a pile length of 18 mm after polish finishing to obtain the high pile.

(Production Example 2)

The drawn yarn obtained in Production Example 1 was relaxed at 5% at 110°C. Further, a high pile was prepared from the relaxed fiber in the same manner as in Production Example 1.

(Production Example 3)

A pressure polymerization reactor having an internal volume of 20 L was charged with 200 parts of ion exchange water, 1.1 parts of sodium lauryl sulfate, 0.13 part of sulfurous acid, 0.17 part of sodium hydrogensulfate, 0.002 part of iron sulfate, 10.7 parts of acrylonitrile and 4.4 parts of vinylidene chloride, and the internal

atmosphere was replaced with nitrogen. The polymerization reactor was adjusted to an internal temperature of 55°C, and charged with 0.012 part of ammonium persulfate as an initiator to initiate polymerization. Polymerization was carried out for a polymerization time of 6 hours and 10 minutes while adding 42.7 parts of acrylonitrile, 41.0 parts of vinylidene chloride, 1.2 parts of sodium styrenesulfonate and 0.135 part of ammonium persulfate. Then, the latex was removed from the polymerization reactor, salted out, treated with heat, filtered, washed with water, dehydrated, and dried to obtain a polymer 3. The polymer 3 was dissolved in acetone to prepare a polymer 3 solution having a polymer 3 concentration of 30 wt%. The polymer 3 solution was mixed with the polymer 2 solution prepared in Production Example 1 at a ratio of the polymer 3 to the polymer 2 of 9:1 to prepare a spinning solution. The resulting spinning solution was discharged through a spinneret with 8,500 holes having a diameter of 0.08 mm into a 30 wt% aqueous acetone solution at 25°C, drawn at a ratio of 2.0 in a 20 wt% aqueous acetone solution at 25°C, and then washed with water at 60°C. Then, the spinning solution was dried at 130°C and further drawn at a ratio of 1.8 at 105°C to obtain a 4.4 dtex drawn yarn. The drawn yarn was relaxed at 5% at 110°C. Further, a high pile was prepared from the

relaxed fiber in the same manner as in Production Example 1.

(Production Example 4)

A pressure polymerization reactor having an internal volume of 5 L was charged with 187 parts of acetone, 47 parts of water, 40 parts of AN, 55 parts of MA and 5 parts of SAM. The components were polymerized in the same manner as in Production Example 1 for the polymer 2 to obtain a solution of a polymer 4. The polymer 1 obtained in Production Example 1 was dissolved in acetone to prepare a polymer 1 solution having a polymer 1 concentration of 30 wt%. The polymer 1 solution was mixed with the polymer 4 solution at a ratio of the polymer 1 to the polymer 4 of 7:3 to prepare a spinning solution. The resulting spinning solution was spun in the same manner as in Production Example 1 to obtain a drawn yarn. A high pile was prepared from the resulting drawn yarn in the same manner as in Production Example 1.

(Production Example 5)

The drawn yarn obtained in Production Example 4 was relaxed at 5% at 110°C. Further, a high pile was prepared from the relaxed fiber in the same manner as in Production Example 1.

(Production Example 6)

The polymer 3 prepared in Production Example 3 was dissolved in acetone to prepare a polymer 3 solution having a polymer 3 concentration of 30 wt%. The polymer

3 solution was mixed with the polymer 4 solution prepared in Production Example 4 at a ratio of the polymer 3 to the polymer 4 of 7:3 to prepare a spinning solution. A relaxed fiber was prepared from the resulting spinning solution in the same manner as in Production Example 3. Next, a high pile was prepared from the relaxed fiber in the same manner as in Production Example 1.

(Production Example 7)

A pressure polymerization reactor having an internal volume of 5 L was charged with 187 parts of acetone, 47 parts of water, 30 parts of AN, 55 parts of MA and 15 parts of SAM. The components were polymerized in the same manner as in Production Example 1 for the polymer 2 to obtain a solution of a polymer 5. The polymer 1 obtained in Production Example 1 was dissolved in acetone to prepare a polymer 1 solution having a polymer 1 concentration of 30 wt%. The polymer 1 solution was mixed with the polymer 5 solution at a ratio of the polymer 1 to the polymer 5 of 9:1 to prepare a spinning solution. The resulting spinning solution was spun in the same manner as in Production Example 1 to obtain a drawn yarn. A high pile was prepared from the resulting drawn yarn in the same manner as in Production Example 1.

(Production Example 8)

The drawn yarn obtained in Production Example 7 was relaxed at 5% at 110°C. Further, a high pile was

prepared from the relaxed fiber in the same manner as in Production Example 1.

(Production Example 9)

A pressure polymerization reactor having an internal volume of 5 L was charged with 187 parts of acetone, 47 parts of water, 60 parts of AN, 25 parts of MA and 15 parts of SAM. The components were polymerized in the same manner as in Production Example 1 for the polymer 2 to obtain a solution of a polymer 6. The polymer 1 obtained in Production Example 1 was dissolved in acetone to prepare a polymer 1 solution having a polymer 1 concentration of 30 wt%. The polymer 1 solution was mixed with the polymer 6 solution at a ratio of the polymer 1 to the polymer 6 of 9:1 to prepare a spinning solution. The resulting spinning solution was spun in the same manner as in Production Example 1 to obtain a drawn yarn. A high pile was prepared from the resulting drawn yarn in the same manner as in Production Example 1.

(Production Example 10)

The drawn yarn obtained in Production Example 9 was relaxed at 5% at 110°C. Further, a high pile was prepared from the relaxed fiber in the same manner as in Production Example 1.

(Production Example 11)

A pressure polymerization reactor having an internal volume of 5 L was charged with 140 parts of acetone, 94 parts of water, 10 parts of AN, 60 parts of methyl

acrylate (hereinafter referred to as MA) and 30 parts of SAM. The components were polymerized in the same manner as in Production Example 1 for the polymer 2 to obtain a solution of a polymer 7. The polymer 1 obtained in Production Example 1 was dissolved in acetone to prepare a polymer 1 solution having a polymer 1 concentration of 30 wt%. The polymer 1 solution was mixed with the polymer 7 solution at a ratio of the polymer 1 to the polymer 7 of 96:4 to prepare a spinning solution. The resulting spinning solution was spun in the same manner as in Production Example 1 to obtain a drawn yarn. A high pile was prepared from the resulting drawn yarn in the same manner as in Production Example 1.

(Production Example 12)

The drawn yarn obtained in Production Example 11 was relaxed at 5% at 110°C. Further, a high pile was prepared from the relaxed fiber in the same manner as in Production Example 1.

(Production Example 13)

A pressure polymerization reactor having an internal volume of 5 L was charged with 187 parts of acetone, 47 parts of water, 50 parts of AN, 35 parts of ethyl acrylate (hereinafter referred to as EA) and 15 parts of SAM. The components were polymerized in the same manner as in Production Example 1 for the polymer 2 to obtain a solution of a polymer 8. The polymer 1 obtained in Production Example 1 was dissolved in acetone to prepare

a polymer 1 solution having a polymer 1 concentration of 30 wt%. The polymer 1 solution was mixed with the polymer 8 solution at a ratio of the polymer 1 to the polymer 8 of 9:1 to prepare a spinning solution. The resulting spinning solution was spun in the same manner as in Production Example 1 to obtain a drawn yarn. A high pile was prepared from the resulting drawn yarn in the same manner as in Production Example 1.

(Production Example 14)

The drawn yarn obtained in Production Example 11 was relaxed at 5% at 110°C. Further, a high pile was prepared from the relaxed fiber in the same manner as in Production Example 1.

(Production Example 15)

A pressure polymerization reactor having an internal volume of 5 L was charged with 187 parts of acetone, 47 parts of water, 50 parts of AN, 35 parts of methyl methacrylate (hereinafter referred to as MMA) and 15 parts of SAM. The components were polymerized in the same manner as in Production Example 1 for the polymer 2 to obtain a solution of a polymer 9. The polymer 1 obtained in Production Example 1 was dissolved in acetone to prepare a polymer 1 solution having a polymer 1 concentration of 30 wt%. The polymer 1 solution was mixed with the polymer 9 solution at a ratio of the polymer 1 to the polymer 9 of 9:1 to prepare a spinning solution. The resulting spinning solution was spun in

the same manner as in Production Example 1 to obtain a drawn yarn. A high pile was prepared from the resulting drawn yarn in the same manner as in Production Example 1.

(Production Example 16)

The drawn yarn obtained in Production Example 13 was relaxed at 5% at 110°C. Further, a high pile was prepared from the relaxed fiber in the same manner as in Production Example 1.

(Production Example 17)

A pressure polymerization reactor having an internal volume of 5 L was charged with 187 parts of acetone, 47 parts of water, 50 parts of AN, 25 parts of MA, 10 parts of vinylidene chloride (hereinafter referred to as VD) and 15 parts of SAM. The components were polymerized in the same manner as in Production Example 1 for the polymer 2 to obtain a solution of a polymer 10. The polymer 1 obtained in Production Example 1 was dissolved in acetone to prepare a polymer 1 solution having a polymer 1 concentration of 30 wt%. The polymer 1 solution was mixed with the polymer 10 solution at a ratio of the polymer 1 to the polymer 10 of 9:1 to prepare a spinning solution. The resulting spinning solution was spun in the same manner as in Production Example 1 to obtain a drawn yarn. A high pile was prepared from the resulting drawn yarn in the same manner as in Production Example 1.

(Production Example 18)

The drawn yarn obtained in Production Example 17 was relaxed at 5% at 110°C. Further, a high pile was prepared from the relaxed fiber in the same manner as in Production Example 1.

The production processes of the fibers obtained in Production Examples 1 to 18 are shown in Table 1.

[Table 1]

	Base polymer composition		Blend polymer composition		Blend Composition Blend polymer/Base polymer	Relaxation treatment
Pro. Ex. 1	Polymer 1	AN^{50}-$VC^{49.5}$-$3S^{0.5}$	Polymer 2	AN^{40}-MA^{45}-SAM^{15}	10/90	0%
Pro. Ex. 2	Polymer 1	AN^{50}-$VC^{49.5}$-$3S^{0.5}$	Polymer 2	AN^{40}-MA^{45}-SAM^{15}	10/90	5%
Pro. Ex. 3	Polymer 3	AN^{50}-$VD^{49.5}$-$3S^{0.5}$	Polymer 2	AN^{40}-MA^{45}-SAM^{15}	10/90	5%
Pro. Ex. 4	Polymer 1	AN^{50}-$VC^{49.5}$-$3S^{0.5}$	Polymer 4	AN^{40}-MA^{55}-SAM^{5}	30/70	0%
Pro. Ex. 5	Polymer 1	AN^{50}-$VC^{49.5}$-$3S^{0.5}$	Polymer 4	AN^{40}-MA^{55}-SAM^{5}	30/70	5%
Pro. Ex. 6	Polymer 3	AN^{50}-$VD^{49.5}$-$3S^{0.5}$	Polymer 4	AN^{40}-MA^{55}-SAM^{5}	30/70	5%
Pro. Ex. 7	Polymer 1	AN^{50}-$VC^{49.5}$-$3S^{0.5}$	Polymer 5	AN^{30}-MA^{55}-SAM^{15}	10/90	0%
Pro. Ex. 8	Polymer 1	AN^{50}-$VC^{49.5}$-$3S^{0.5}$	Polymer 5	AN^{30}-MA^{55}-SAM^{15}	10/90	5%
Pro. Ex. 9	Polymer 1	AN^{50}-$VC^{49.5}$-$3S^{0.5}$	Polymer 6	AN^{60}-MA^{25}-SAM^{15}	10/90	0%
Pro. Ex. 10	Polymer 1	AN^{50}-$VC^{49.5}$-$3S^{0.5}$	Polymer 6	AN^{60}-MA^{25}-SAM^{15}	10/90	5%
Pro. Ex. 11	Polymer 1	AN^{50}-$VC^{49.5}$-$3S^{0.5}$	Polymer 7	AN^{10}-MA^{60}-SAM^{30}	4/96	0%
Pro. Ex. 12	Polymer 1	AN^{50}-$VC^{49.5}$-$3S^{0.5}$	Polymer 7	AN^{10}-MA^{60}-SAM^{30}	4/96	5%
Pro. Ex. 13	Polymer 1	AN^{50}-$VC^{49.5}$-$3S^{0.5}$	Polymer 8	AN^{50}-EA^{35}-SAM^{15}	10/90	0%
Pro. Ex. 14	Polymer 1	AN^{50}-$VC^{49.5}$-$3S^{0.5}$	Polymer 8	AN^{50}-EA^{35}-SAM^{15}	10/90	5%
Pro. Ex. 15	Polymer 1	AN^{50}-$VC^{49.5}$-$3S^{0.5}$	Polymer 9	AN^{50}-MA^{35}-SAM^{15}	10/90	0%
Pro. Ex. 16	Polymer 1	AN^{50}-$VC^{49.5}$-$3S^{0.5}$	Polymer 9	AN^{50}-MA^{35}-SAM^{15}	10/90	5%
Pro. Ex. 17	Polymer 1	AN^{50}-$VC^{49.5}$-$3S^{0.5}$	Polymer 10	AN^{50}-MA^{25}-VD^{10}-SAM^{15}	10/90	0%
Pro. Ex. 18	Polymer 1	AN^{50}-$VC^{49.5}$-$3S^{0.5}$	Polymer 10	AN^{50}-MA^{25}-VD^{10}-SAM^{15}	10/90	5%

(Examples 1 to 16)

The shrinkable fibers obtained in Production Examples 1, 2, 4, 5, 7 to 18 were dyed at 60°C, 70°C and 80°C for 60 minutes. The relative saturation values, dyeing shrinkage percentages and shrinkage percentages after dyeing at that time are shown in Table 2. When the spinning solution is incompatible, the dyeing shrinkage percentage is 10% or less and the shrinkage percentage after dyeing is 20% or more in dyeing at 60 to 80°C; the relative saturation value is 0.1 or more in dyeing at 60° or more; and the relative saturation value is 0.8 or more in dyeing at 70°C or more.

Further, appearance of the high piles obtained in Production Examples 1, 2, 4, 5, 7 to 18 was evaluated. The results are shown in Table 2. When the shrinkage percentage after dyeing is 20% or more, a high pile having appearance characteristics in which the step between the long pile part and the short pile part is emphasized can be obtained.

(Comparative Examples 1 and 2)

The shrinkable fibers obtained in Production Examples 3 and 6 were dyed at 60°C, 70°C and 80°C for 60 minutes. The relative saturation values, dyeing shrinkage percentages and shrinkage percentages after dyeing at that time are shown in Table 2.

When the spinning solution is compatible, it is difficult to make the dyeing shrinkage percentage 10% or less in dyeing at 70 to 80°C.

Further, appearance of the high piles obtained in Production Examples 3 and 6 was evaluated. The results are shown in Table 2. When the shrinkage percentage after dyeing is 20% or less, the step between the long pile part and the short pile part almost cannot be observed.

[Table 2]

	Production process	Phase separation state (μm)	Relative saturation value			Dyeing shrinkage percentage (%)			Shrinkage percentage after dyeing (%)			High pile appearance evaluation		
			Dyeing temperature (°C)			Dyeing temperature (°C)			Dyeing temperature (°C)			Dyeing temperature (°C)		
			60	70	80	60	70	80	60	70	80	60	70	80
Ex. 1	Pro. Ex. 1	10	0.2	1.0	-	2	7	-	36	30	-	VG	VG	-
Ex. 2	Pro. Ex. 2	10	-	-	2.2	-	-	7	-	-	24	-	-	G
Com. Ex. 1	Pro. Ex. 3	compatible	0.3	1.0	2.3	8	19	30	30	21	10	VG	G	P
Ex. 3	Pro. Ex. 4	7	0.3	1.1	-	3	9	-	37	32	-	VG	VG	-
Ex. 4	Pro. Ex. 5	7	-	-	2.4	-	-	8	-	-	26	-	-	G
Com. Ex. 2	Pro. Ex. 6	compatible	0.4	1.3	2.5	9	20	35	28	18	5	VG	P	P
Ex. 5	Pro. Ex. 7	9	0.3	1.0	-	2	8	-	36	31	-	VG	VG	-
Ex. 6	Pro. Ex. 8	9	-	-	2.1	-	-	8	-	-	24	-	-	G
Ex. 7	Pro. Ex. 9	11	0.2	0.8	-	2	6	-	35	30	-	VG	VG	-
Ex. 8	Pro. Ex. 10	11	-	-	1.9	-	-	6	-	-	24	-	-	G
Ex. 9	Pro. Ex. 11	12	0.1	0.8	-	2	6	-	36	31	-	VG	VG	-
Ex. 10	Pro. Ex. 12	12	-	-	2.2	-	-	7	-	-	24	-	-	G
Ex. 11	Pro. Ex. 13	11	0.2	0.9	-	2	5	-	34	29	-	VG	VG	-
Ex. 12	Pro. Ex. 14	11	-	-	1.8	-	-	7	-	-	23	-	-	G
Ex. 13	Pro. Ex. 15	6	0.1	0.8	-	2	5	-	34	29	-	VG	VG	-
Ex. 14	Pro. Ex. 16	6	-	-	1.8	-	-	6	-	-	22	-	-	G
Ex. 15	Pro. Ex. 17	6	0.1	0.8	-	1	6	-	34	28	-	VG	VG	-
Ex. 16	Pro. Ex. 18	6	-	-	1.7	-	-	6	-	-	21	-	-	G

Industrial Applicability

The acrylic shrinkable fiber of the present invention only slightly shrinks when dyed, and has a high shrinkage percentage even after drying. As a result, new goods in wide range of applications such as clothes, toys (such as stuffed toys) and interior goods using the fiber can be planned.